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The wash-off of dyeings using interstitial water: Part 3. Disperse dyes on polyester

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ABSTRACT

Poly(ethylene terephthalate), which had been dyed at 0.5, 1.0 and 2.0% omf depths of shade using three disperse dyes, was reduction cleared using a traditional, four-stage process that comprised two water rinses at 40 °C, treatment with aq $Na_2CO_3/Na_2S_2O_4$ at 60 °C and one cold water rinse. A novel, two-stage wash-off method was also employed that consisted of treatment with damp nylon beads and surfactant at 70 °C and one cold water rinse. In terms of fastness to repeated washing at 60 °C and colorimetric characteristics, the traditional, four-stage reduction clearing treatment using aq., alkaline $Na_2S_2O_4$ could be replaced by the two-stage, bead wash-off with detergent at 70 °C. As the detergent-based, bead wash-off process used lower amounts of water than reduction clearing and did not employ sodium dithionite, it avoided the environmentally unacceptable generation of aromatic amines in the case of the reduction clearing of azo dyes. Calculations indicated that considerably less heat energy was consumed in bead wash-off than reduction clearing not only because two, rather than four stages were involved but also since the bead process used only a 2:1 water:fibre ratio rather than the 20:1 liquor ratio employed in the reduction clear process; also, the much lower specific heat capacity of nylon than water meant that much less heat was required to heat the beads. The beads adsorbed vagrant disperse dye during wash-off, thereby offering the potential of a lower effluent load compared to a traditional reduction clearing treatment for disperse dyes on polyester.

1. Introduction

Surplus dye and dyeing/printing auxiliaries are removed from dyeings and prints by means of an aqueous treatment, to which the generic term ‘wash-off’ has been ascribed [1]. In the case of poly (ethylene terephthalate) (PET) and other hydrophobic fibres, such as poly(lactic acid) (PLA) which has been dyed with disperse dyes, particulate dye molecules accumulate at the fibre surface at the end of dyeing because of the dye’s sparing solubility in water. As this surface deposited dye impairs brightness of shade and reduces fastness, a specific wash-off process, commonly referred to as *reduction clearing* is employed, which entails treating the dyed material at 50–80 °C in an aqueous, alkaline solution of sodium dithionite (sodium hydrosulfite; $Na_2S_2O_4$). In the case of azo disperse dyes, the typically, 4–5 stage reduction clearing process, such as that shown in Fig. 1, cleaves the azo bond, generating colourless amino compounds whilst anthraquininoid disperse dyes are converted to the almost colourless, water-soluble, low substantivity, *leuco* variant (Scheme 1). The ability of the reduction clearing process to reduce dye that is present only at the fibre surface accrues from the marked hydrophobicity of the fibres (e.g. PET, PLA) which are traditionally dyed using disperse dyes together with the fact that the process is carried out below the glass transition temperature (T_g) of the fibre (for example, ~55–65 °C for PLA and ~80–90 °C for PET, respectively), with the result that the aqueous alkaline, $Na_2S_2O_4$ solution does not penetrate the fibre. Reduction clearing is widely used, especially in the case of medium/heavy depths of shade and, for some forms of dyed polyester, regardless of depth of shade, to remove surface deposited polyester oligomers [2].

However, reduction clearing suffers from several disadvantages insofar as the multi-stage process necessitates three changes in pH [acidic dyebath (~pH 5) to alkaline reduction clear (~pH 12) to neutralisation with aq. CH_3COOH] and also consumes large amounts of water, energy and chemicals; in addition, sodium dithionite generates an environmentally unacceptable effluent that is further compromised by the presence of aromatic amines in the case of azo disperse dyes. Attempts have been made to reduce the environmental impact and cost of reduction clearing, as exemplified by research efforts directed towards temporarily solubilised disperse dyes [3–16], microencapsulated disperse dyes [17], and, in the late 1970’s, the introduction of commercial ranges of alkali-clearable disperse dyes [18–20], which, under hot, aq. alkaline conditions, either generate water-soluble derivatives via hydrolysis or undergo decolourisation via cleavage of the chromophoric system, thereby enabling surface

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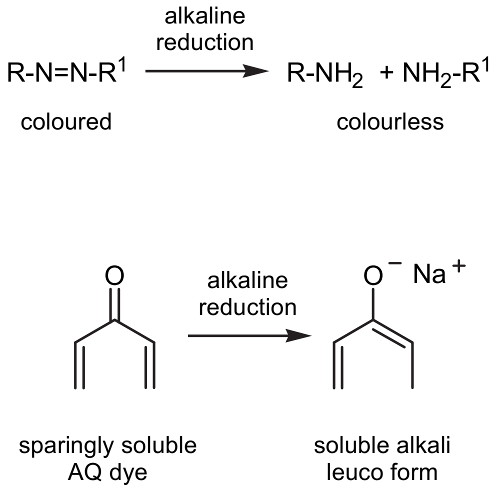
deposited disperse dye to be removed without recourse to reducing agents; alkali-clearable disperse dyes continue to attract research attention [7–9,11–13,15,21–31]. Various replacements to sodium dithionite have been investigated, including acetone [32], ozone [25,33] and detergents [34–37], the latter approach having been shown [34] to not only reduce the BOD, COD, TOC and suspended solids generated during a typical traditional reduction clearing treatment of disperse dyes on polyester but also to offer a potential way of avoiding the environmentally unacceptable generation of aromatic amines in the case of azo dyes. However, despite such interest, the traditional reduction clearing process using aq. alkaline, $Na_2S_2O_4$ treatment continues to enjoy widespread use, mostly in unchanged guise since its inception in the mid 1950's [38,39].

This paper describes the use of a wash-off process for dyeings that employs a novel, re-usable and re-cyclable polyamide bead medium to replace the vast majority of the water and chemicals that are traditionally used in wash-off. The patented, novel process [40], which is currently being commercialised by Xeros Ltd. [41] does not employ a large reservoir of water to immerse the dyeing/print but, rather, uses only the relatively small amount of water present within the interstices of both the damp fabric and the bead material. The first part of the paper [42] comprised an introduction to the wash-off process, describing the theoretical and empirical considerations that underpinned the selection of the nylon bead material whilst the second part of the paper [43] compared the wash-off of 2% and 5% omf dyeings of bis(aminochlorotriazine) dyes reactive dyes from cotton, using the dye maker's recommended, five- and six-stage, wash-off processes as well as a novel method that utilised two water rinses and treatment with damp nylon beads. Similar depths of shade of comparable fastness to repeated wash fastness at 60 °C were achieved using the various wash-off methods [43]. As the beads adsorbed a sizeable amount of vagrant reactive dye that was removed during wash-off, the bead wash-off process generated less rinse liquor compared than the recommended wash-off processes, thereby constituting a lower effluent load [43]. This part of the paper describes the use of the novel, bead wash-off process for PET which had been dyed with disperse dyes and compares the colorimetric and fastness data secured for the washed-off dyeings to those which had been obtained in a previous study [34] using a traditional reduction clearing process.

2. Experimental

2.1. Materials

Scoured, woven polyester fabric (122 g m^{-2}; Whaleys) together with commercial samples of the three disperse dyes, namely *Dianix Blue UN-SE*, *Dianix Yellow Brown XF and Dianix Cherry CC* (no C.I. Generic Names ascribed), were used. Commercial samples of the non-ionic surfactant, *Sandozin NIN* was kindly supplied by Clariant, the proprietary anionic levelling agent *Levegal DLP* from DyStar and *ECE Reference Detergent B* from SDC Enterprises Ltd. Owing to commercial confidentiality, details of the polyamide bead material used cannot be disclosed.



Scheme 1. Effect of reduction clearing on azo and AQ disperse dyes.

2.2. Dyeing

0.5, 1.0 and 2.0% omf depths of shade were carried out in sealed, 300 cm^3 capacity, stainless steel dyepots housed in a Roaches *Pyrotec S* dyeing machine, employing a 20:1 liquor ratio (Fig. 2); the pH was adjusted using McIlvaine buffer [44].

2.3. Reduction clearing

After dyeing, the fabrics were reduction cleared using the method shown in Fig. 3, employing a 20:1 liquor ratio. The rinsed, reduction cleared dyeings were allowed to dry in the open air.

2.4. Bead wash-off

Dyeings were squeezed and treated, using the method shown in Fig. 4, in a sealed polypropylene container using sufficient beads to provide a 1:15 dyed fabric:bead ratio and sufficient aq 4 gl^{-1}

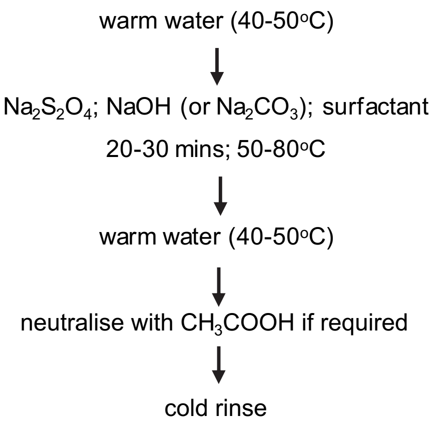


Fig. 1. Typical reduction clearing process for disperse dyes on hydrophobic fibres.

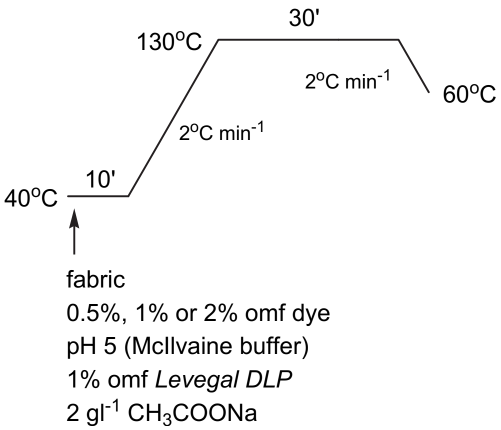


Fig. 2. Dyeing method.

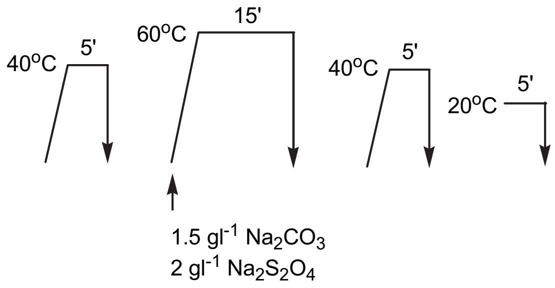


Fig. 3. Reduction clearing method.

Sandozin NIN or 4 gl^{-1} ECE detergent solution to provide a 2:1 liquor ratio. The rinsed, treated dyeings were allowed to dry in the open air.

2.5. Colour measurement

2.5.1. Dyed fabric

The methods and equipment described previously [34] were used; dyed samples were folded so as to realise four thicknesses.

2.5.2. Beads

A black plastic tube (10 mm in length and 30 mm in diameter) terminated at one end by a glass plate, was filled with beads and a white disc was then fastened in place over the remaining open end. The glass plate of the sealed tube was placed against the 30 mm viewing aperture of a *Datacolor Spectroflash 600* spectrophotometer and the CIE colorimetric co-ordinates and fk values of the beads were calculated from the reflectance values at the appropriate λ_{max} measured under illuminant D_{65}, employing a 10° standard observer with UV component included and specular component excluded.

2.6. Fastness determination

The wash fastness of the dyed samples to five, consecutive wash tests was determined at 60 °C, using the ISO standard wash test (ISO CO6/C2S) [45] which had been modified in that dyeings were subjected to five, consecutive wash tests and, at the end of each wash test, the washed sample was rinsed thoroughly in tap water (but was not dried) and a fresh sample of SDC multifibre strip was used to assess the extent of staining for each of the five wash tests.

3. Results and discussion

3.1. Background

As discussed previously [34], the three dyes used were chosen arbitrarily as being representative of typical, modern disperse dyes; *Blue UN-SE* is a mixture of azo and AQ dyes while *Yellow Brown XF* and *Cherry CC* are azo dyes. Three depths of shade were used namely, 0.5%, 1% and 2% omf, as these provided typical pale/medium depth dyeings. The results displayed in Figs. 5–9 for the dyeings both before and after reduction clearing were reported in a previous study [34] that compared the effectiveness of a traditional, sodium dithionite-based reduction clearing process with a detergent-based wash-off process for three disperse dyes on polyester.

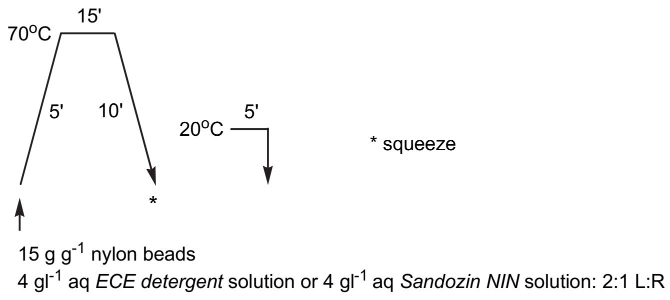


Fig. 4. Nylon bead wash-off method.

3.2. Results obtained prior to reduction clearing

Fig. 5 shows the colorimetric parameters and Fig. 6 the colour strength (K/S values) obtained for 0.5%, 1% and 2% omf dyeings which had received ‘nil’ treatment (ie neither reduction clearing nor bead wash-off) after dyeing. Instead, at the end of dyeing, excess dye liquor had been removed from the dyeings by squeezing and the samples had then been allowed to dry in the open air prior to wash fastness testing. When the ‘nil’ treated dyeings were subjected to five, repeated wash tests at 60 °C, poor fastness was recorded, especially in the cases of the 1% and 2% omf depths of shade, as shown by the shade changes and the high levels of staining of the adjacent nylon 6,6 and polyester fabrics obtained after five repeated washes (Table 1). The finding that both PET and nylon 6,6 adjacent materials were the most heavily stained of the six component fabrics of the multifibre strip during washing (Table 1) was expected, in view of the well-known substantivity of disperse dyes towards these two particular types of fibre [2]. Table 1 also shows that the extent of staining of both PET and polyamide fabrics secured for the 1% and 2% omf dyeings after the first two or so wash tests was worse than that obtained for subsequent wash tests, which can be attributed to the facts that surplus dye had not been removed from the dyeings by a reduction clearing treatment and the first two or so wash tests at 60 °C, removed this surplus dye. The vagrant dye that was removed from the dyeings by repeated wash testing lowered the colour strength of the dyeings, as can be seen by comparing the K/S values obtained for the ‘nil’ treated dyeings before (Fig. 6) and after (Fig. 7) five repeated wash tests. The colorimetric parameters of the dyeings after repeated wash testing are shown in Fig. 8.

3.3. Results obtained using reduction clearing

When the 0.5%, 1% and 2% omf dyeings were reduction cleared, the hot, aq., alkaline solution of sodium dithionite removed surplus dye, resulting in a reduction in the depth of shade of the dyeings, as evidenced by the lower K/S values obtained for the reduction cleared dyeings compared to those of the non-reduction cleared/unwashed-off dyeings before wash testing (Fig. 6). The reduced depth of shade imparted by reduction clearing is also reflected in the lower L^* values recorded for the reduction cleared samples compared to those of the dyeings which had not received a reduction clear (Fig. 5). Reduction clearing had a small effect upon both the hue and chroma of the dyeings, as shown by a comparison of the colorimetric parameters recorded for the ‘nil’ treated dyeings, which had been neither reduction cleared nor bead washed-off, with those which had been subjected to reduction clearing (Fig. 5). The finding (Table 2) that the $\lambda_{max.}$ of the various dyeings were unchanged as a result of reduction provides further evidence that the changes in colour imparted were small.

The colour strength of the reduction cleared dyeings after repeated washing was generally lower than that achieved for the corresponding non-reduction cleared/unwashed-off dyeings after repeated wash testing (Fig. 7), which can be attributed to dye having been removed not only during repeated washing but also

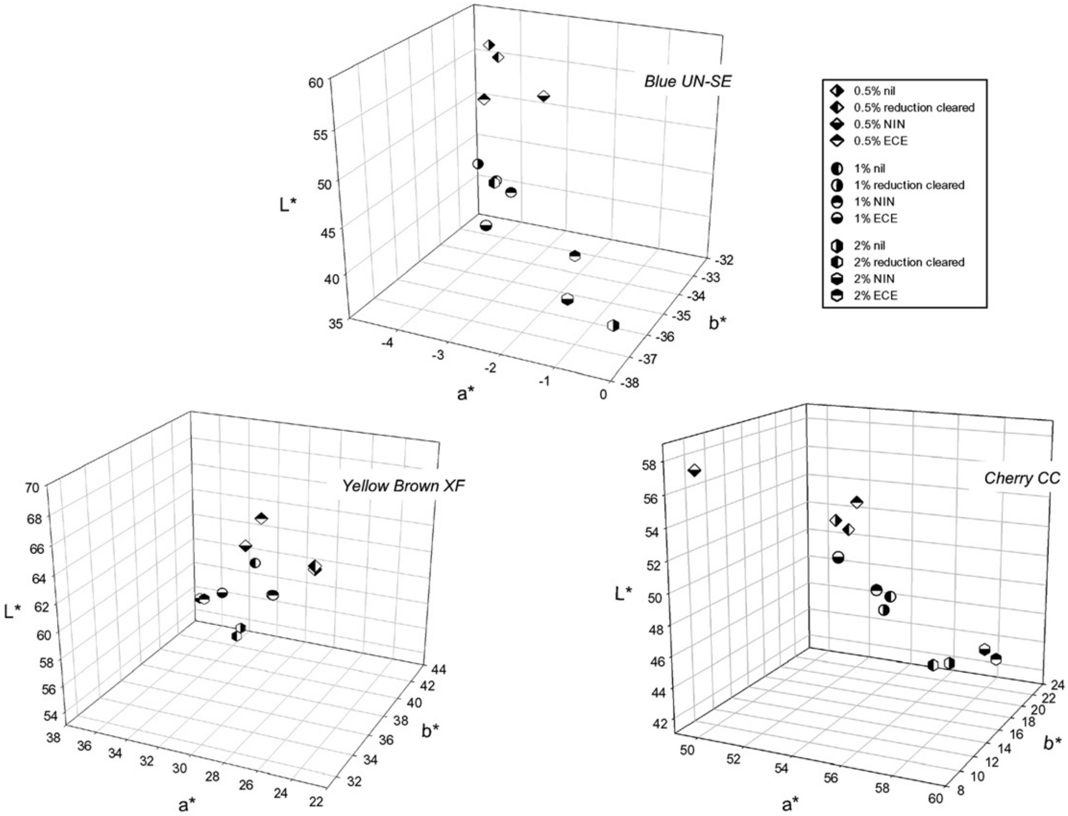


Fig. 5. Colorimetric parameters of dyeings prior to wash testing.

during the reduction clearing process. When the staining and shade change results obtained for the reduction cleared samples after five washes (Table 1) are compared with those obtained for the dyeings which had not been reduction cleared or washed-off (Table 1), it is apparent that the reduction cleared samples displayed higher fastness, especially in the cases of the first two or so washes, owing to the reduction clearing treatment having removed surplus dye from the dyeings prior to repeated wash testing. However, the fastness of both the reduction cleared and non-reduction cleared dyeings was virtually identical after four and five washes (Table 1). It is also clear from Table 1 that in the case of the 2% omf dyeings, the fastness of the reduction cleared dyeings for the first two or so wash tests was generally worse than that secured for subsequent wash tests, which implies that

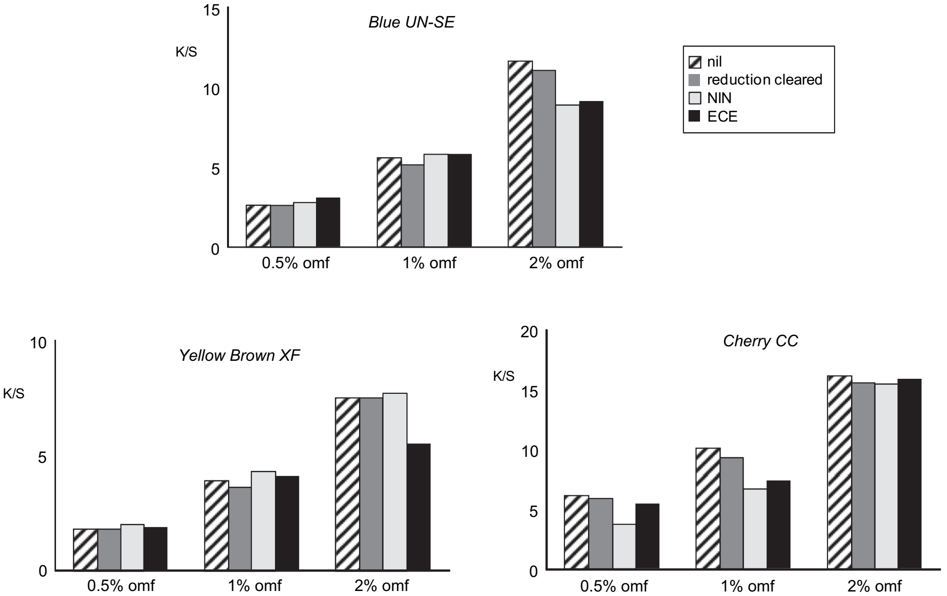


Fig. 6. Colour strength of dyeings prior to wash testing.

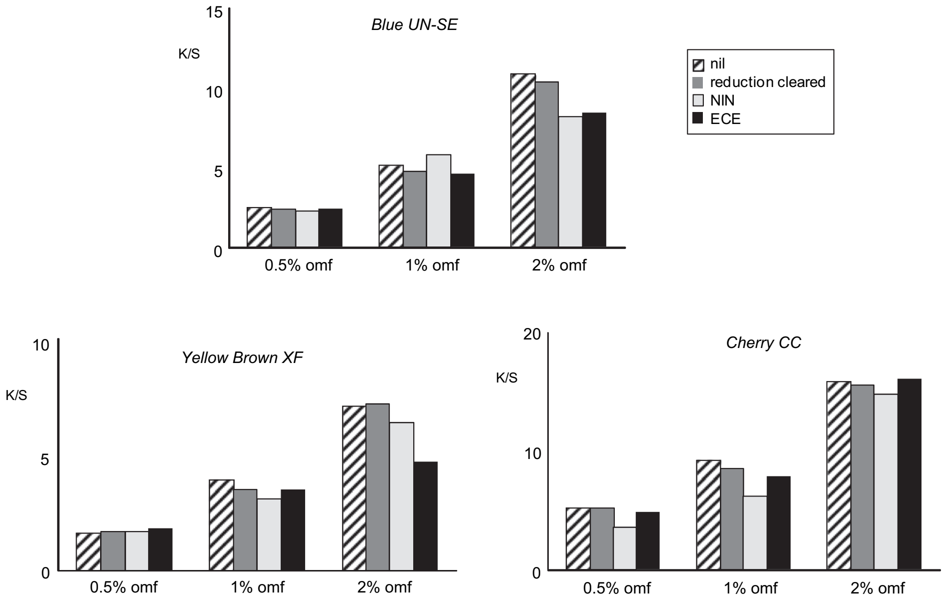


Fig. 7. Colour strength of dyeings after wash testing.

reduction clearing had not removed all surplus dye from the dyeings. Fig. 8 shows that the colour of the dyeings which had been reduction cleared and subjected to repeated wash testing was slightly different to that of the dyeings which had not received reduction clearing/wash-off and which had been wash tested. However, the observation that the $\lambda_{max.}$ values of the various dyeings were identical (Table 2) reveals that these differences in colour were very small.

3.4. Results obtained using beads

As mentioned, the traditional, multi-stage reduction clearing process suffers from the disadvantage that sodium dithionite generates an environmentally unacceptable effluent that is further compromised by the presence of aromatic amines in the case of azo disperse dyes; in addition, the process necessitates three changes in pH namely, acidic dyebath to alkaline reduction clear to

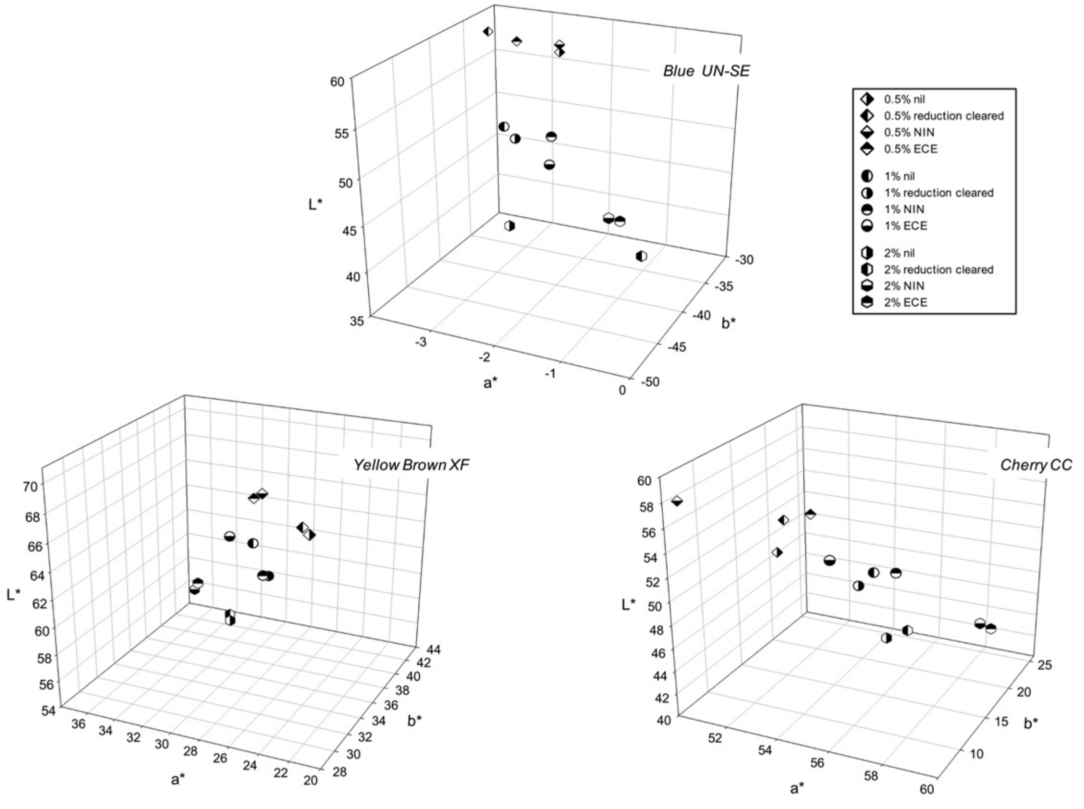


Fig. 8. Colorimetric parameters of dyeings after wash testing.

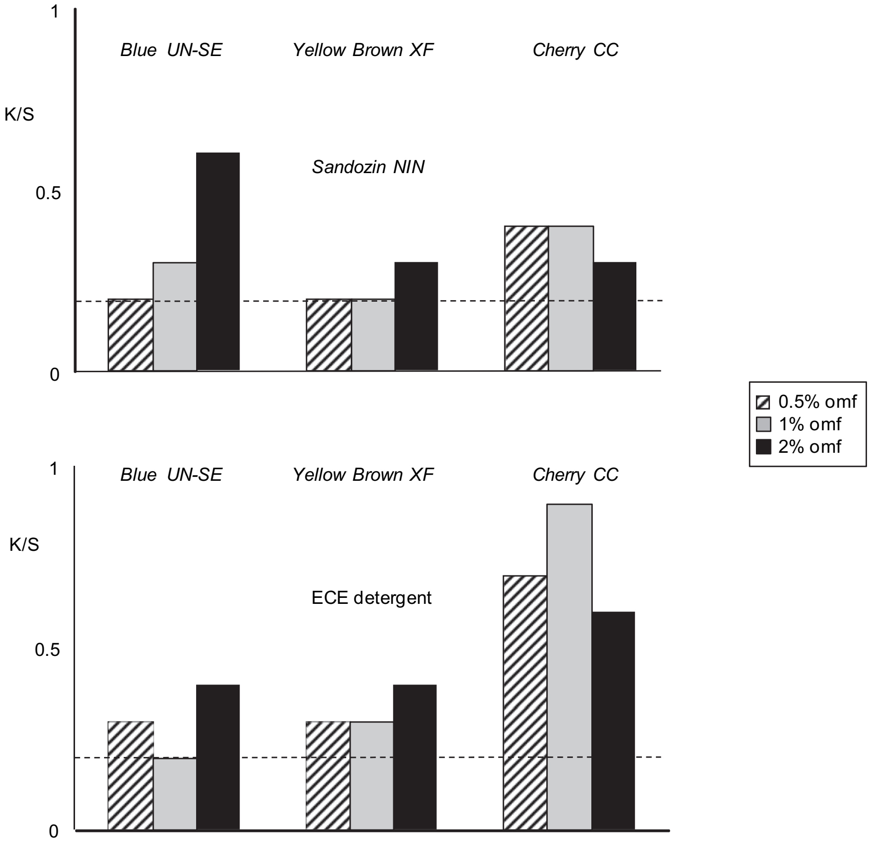


Fig. 9. Colour strength of beads.

neutralisation with CH_3COOH. Previous studies by one of the current authors revealed that, in terms of fastness and colorimetric characteristics, the traditional, hot, aq. alkaline sodium dithionite, reduction clearing process could be replaced with hot, aq. alkaline detergent solution in the cases of both PET [34] and PLA [35] dyed with disperse dyes. However, from the viewpoint of dyed PET, which is of relevance to the work described herein, whilst detergent wash-off enabled a major reduction to be achieved in terms of the BOD, COD and TOC that are typically generated as a result of the traditional reduction clearing, it nevertheless necessitated the use of a boiling aqueous solution of detergent and Na_2CO_3 [34]. In this context, it was decided to examine the possibility of employing a detergent-based wash-off process for dyed PET that required neither the use of aq alkali nor treatment with detergent at 98 °C. To this end, two commercial detergent formulations were selected for use, namely:

- *ECE Reference Detergent B (*SDC Enterprises Ltd.), which is used in the ISO CO6 fastness tests [46] and has been employed as an alternative to alkali/$Na_2S_2O_4$ in the traditional reduction clearing of disperse dyes from both PET and PLA [34–37];
- the non-ionic surfactant, *Sandozin NIN* (Clariant) which is a commonly used fibre scouring assistant [37,47,48].

Accordingly, dyeings were squeezed and treated, using the method shown in Fig. 4, in a sealed polypropylene container, employing sufficient beads to provide a 1:15 dyed fibre:bead ratio and sufficient aq 4 gl^{-1} *Sandozin NIN* or *ECE Detergent* solution to provide a 2:1 detergent:dyed fibre ratio. At the end of this treatment, the dyeing was removed and rinsed in cold water for 5 min prior to drying.

Fig. 5 shows that the two bead wash-off processes (i.e. *Sandozin NIN* and *ECE detergent*) imparted similar, slight changes to the colour of the dyeings and that these changes were of a similar magnitude to those imparted by reduction clearing; the finding (Table 2) that the $\lambda_{max.}$ values of the various dyeings were identical reveals that these differences in colour were very small. Fig. 6 reveals that treatment of the 0.5%, 1% and 2% omf dyeings with the *Sandozin NIN* and *ECE detergent* wash-off methods prior to wash testing, did not necessarily result in a reduction in the depth of shade of the dyeings, as indicated by lower K/S values compared to those of the non-reduction cleared/unwashed-off dyeings. Indeed, Fig. 6 shows that for some of the dyeings, the 70 °C bead treatment resulted in increased K/S; it is also apparent that the two detergent formulations differed in their effects upon colour strength. As such, these findings are different to those obtained for reduction clearing, for which it was found that colour strength of the dyeings was reduced prior to dyeing (Fig. 6) and can best be explained by reference to the likely mechanism by which the bead wash-off removes surplus dye.

An investigation [49] into the nature by which the new bead wash-off process functions in the cases of dyes and stains on various textile fibres revealed that the beads remove surplus dye from the surface of the dyeing as a result of their physical contact with the wetted-out material. In essence, during bead wash-off, dye molecules at the surface of the dyeing are removed through contact with and adsorption onto, the beads. Additional, mobile dye molecules situated at or near to the fibre surface, migrate, so as to replace the desorbed dye molecules and, such migrated dye molecules are themselves subsequently removed by contact with beads; the processes of dye desorption and dye migration continue until either no further mobile dye molecules are available for removal from the

Table 1
Fastness to repeated washing of dyeings (nil = no reduction clear or wash-off; RC = reduction cleared; NIN = *Sandozin NIN*; ECE = ECE detergent).

Dye	% omf	No. of washes	Shade change				Staining of adjacent multifibre strip materials																							
			nil	RC	NIN		Wool				Acrylic				Polyester				Nylon				Cotton				2° acetate			
						ECE	Nil	RC	NIN	ECE	Nil	RC	NIN	ECE	Nil	RC	NIN	ECE	Nil	RC	NIN	ECE	Nil	RC	NIN	ECE	Nil	RC	NIN	ECE
Blue UN-SE	0.5	1	–	–	–	–	5	5	5	5	5	5	5	5	5	5	5	5	4/5	4/5	4/5	4/5	5	5	5	5	5	5	5	5
		2	–	–	–	–	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
		3	–	–	–	–	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
		4	–	–	–	–	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
		5	4/5	4/5	4/5	4/5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
	1	1	–	–	–	–	5	5	5	5	5	5	5	5	4/5	5	4/5	4/5	3/4	4/5	4/5	4/5	5	5	5	5	5	5	5	5
		2	–	–	–	–	5	5	5	5	5	5	5	5	5	5	5	5	4/5	5	4/5	5	5	5	5	5	5	5	5	5
		3	–	–	–	–	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
		4	–	–	–	–	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
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		4	–	–	–	–	5	5	5	5	5	5	5	5	5	5	4/5	5	4/5	5	4/5	4/5	5	5	5	5	5	5	5	5
		5	3/4	4/5	4/5	4/5	5	5	5	5	5	5	5	5	5	5	4/5	5	4/5	4/5	5	5	5	5	5	5	5	5	5	5
Yellow Brown XF	0.5	1	–	–	–	–	4	5	5	5	5	5	5	5	5	5	5	5	4/5	4/5	5	5	5	5	5	5	4/5	5	5	5
		2	–	–	–	–	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
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		3	–	–	–	–	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
		4	–	–	–	–	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
		5	4/5	4/5	4/5	4/5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Cherry CC	0.5	1	–	–	–	–	5	5	5	5	5	5	5	5	4	5	4/5	5	3	4	4	4/5	5	5	5	5	4	4/5	4/5	5
		2	–	–	–	–	5	5	5	5	5	5	5	5	5	5	5	5	4/5	5	4/5	5	5	5	5	5	5	5	5	5
		3	–	–	–	–	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4/5	5	5	5	5	5	5	5	5	5
		4	–	–	–	–	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4/5	5	5	5	5	5	5	5	5	5
		5	3/4	4/5	4	4/5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4/5	5	5	5	5	5	5	5	5	5
	1	1	–	–	–	–	4/5	5	5	4/5	5	5	5	5	4	4/5	4/5	4	2/3	3/4	3/4	3/4	4	5	5	5	3	4/5	4	3/4
		2	–	–	–	–	5	5	5	5	5	5	5	5	5	5	5	5	4/5	4/5	4/5	4/5	5	5	5	5	5	5	5	4/5
		3	–	–	–	–	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4/5	4/5	5	5	5	5	5	5	5	5
		4	–	–	–	–	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4/5	4/5	5	5	5	5	5	5	5	5
		5	3/4	3/4	3/4	3/4	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4/5	4/5	5	5	5	5	5	5	5	5
	2	1	–	–	–	–	4	4/5	5	5	5	5	5	5	4	4/5	4/5	4/5	2	2/3	4	4	4	5	5	5	3	3/4	5	4
		2	–	–	–	–	5	5	5	5	5	5	5	5	5	5	5	5	4	4	4/5	4/5	5	5	5	5	4/5	5	5	5
		3	–	–	–	–	5	5	5	5	5	5	5	5	5	5	5	5	4/5	4/5	4/5	5	5	5	5	5	5	5	5	5
		4	–	–	–	–	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4/5	5	5	5	5	5	5	5	5	5
		5	3	3/4	3	3/4	5	5	5	5	5	5	5	5	5	5	5	5	5	5	4/5	5	5	5	5	5	5	5	5	5

dyed surface or the wash-off process is halted. The accumulation of dye molecules at the fibre surface that arises because of their migration from within the dyed fibre explains the findings (Fig. 6) that bead wash-off increased the colour strength of several of the 0.5%, 1% and 2% omf dyeings. Evidence that vagrant dye molecules were adsorbed by the beads during wash-off is provided by the results displayed in Fig. 9, which shows the colour strength of the beads prior to wash-off (the dashed lines) as well as that of beads which had been used in both the *Sandozin NIN* and ECE detergent wash-off processes and which had been allowed to dry in the open air. Comparison of the K/S of the beads which had been used for wash-off with that of the beads prior to wash-off (the dashed line in Fig. 9) shows that not only has vagrant dye been adsorbed onto the beads but also provides a measure of the extent of this dye adsorption. This particular aspect of the bead wash-off and, in particular, the fact that vagrant dye which is adsorbed onto the surface of the beads diffuses into the interior of the bead and, as a result, the dye is not simply redeposited on other areas of the dyeing was discussed in the second part of this paper [43]. Indeed, a discussion of the re-use of coloured beads which contained adsorbed, residual dye in subsequent wash-off processes was presented earlier [43] in the context of the *Xeros* clothes washing system [41], which can save up to 90% of water usage compared to conventional laundry systems, which employs beads that can be used up to five hundred times before being recycled [50].

Table 1 shows the fastness, to five repeated wash tests at 60 °C, of dyeings which had been subjected to each of the two nylon bead wash-off processes, namely that which employed *Sandozin NIN* and that which used *ECE detergent*. It is apparent, in terms of both shade change and staining of adjacent polyester and nylon multifibre strip materials, that similar levels of fastness were recorded for the two bead wash-off processes and, also, that these levels of fastness were, in turn, similar to those recorded for the reduction cleared dyeings, except in the case of *Cherry CC*, for which the *Sandozin NIN* bead washed-off dyeings were assigned slightly lower (i.e. 0.5 Grey Scale) ratings for staining of adjacent nylon and polyester materials.

Fig. 7 shows that the colour strength of the bead washed-off dyeings after repeated washing differed to that obtained for their reduction cleared counterparts and, also, that these differences varied for the three dyes used. These findings concur with those obtained previously in the cases of both PET [34] and PLA [35–37] dyed with disperse dyes which had been washed-off using aq. detergent solution. It is also clear from Fig. 7 that differences were obtained between the two detergent formulations used in terms of the K/S values of the washed dyeings, although these differences once again varied for the three dyes used. Such differences were anticipated, since the two formulations employed were not intended for disperse dye wash-off and differ markedly in proposed application, namely ISO CO6 fastness testing in the case of *ECE Detergent* and fibre scouring in the case of *Sandozin NIN*. Despite the differences between the two detergent formulations, Fig. 8 reveals that after wash testing, the colour of the dyeings which had been washed-off using the two bead processes was not too dissimilar, although this was different to that of the reduction cleared dyeings insofar as the bead washed-off dyeings were of higher chroma, which could be attributed to reduced aggregation of the disperse dyes imparted by the two detergents used. Nevertheless, the observation (Table 2) that the $\lambda_{max.}$ values of the various dyeings after wash fastness testing were identical shows that these differences in colour were very small.

Table 2
λmax values for dyeings both before and after washing.

Dye	% omf	Number of washes	Treatment	λ_{max}/nm
Blue UN-SE	0.5	0	nil; RC; NIN;ECE	620
		5		620
	1	0	nil; RC; NIN;ECE	620
		5		620
	2	0	nil; RC; NIN;ECE	620
		5		620
Yellow Brown XF	0.5	0	nil; RC; NIN;ECE	460
		5		460
	1	0	nil; RC; NIN;ECE	440
		5		440
	2	0	nil; RC; NIN;ECE	440
		5		440
Cherry CC	0.5	0	nil; RC; NIN;ECE	520
		5		520
	1	0	nil; RC; NIN;ECE	520
		5		520
	2	0	nil; RC; NIN;ECE	520
		5		520

3.5. Energy considerations

From an energy perspective, as the bead wash-off process comprised two stages compared to the four stages of the standard reduction clearing process, it follows that the bead wash-off method should offer potential energy savings. To obtain an approximate measure of the size of the amount of energy used in the two different wash-off processes, Eq. (1) was employed to calculate the amount of heat required (Q; kJ) to raise the temperature of m kg of water from 21 °C (T_1) to the final temperature (T_2; 40 or 60 °C) of the particular stage of reduction clearing process, where c_w is the specific heat capacity of water at 21 °C (4.18 kJ kg^{-1} K^{-1}) and Eq. (2) was used to calculate the heat involved in raising the temperature of n kg of nylon beads from 21 °C (T_1) to T_2 (70 °C), where c_n is the specific heat capacity of nylon 6 at 20 °C (1.67 kJ kg^{-1} K^{-1} [51]):

$$Q = mc_w(T_2 - T_1) \tag{1}$$

$$Q = nc_n(T_2 - T_1) \tag{2}$$

In using Eqs. (1) and (2), no attempts were made to take into account the effects of the various chemicals, substrate, etc upon specific heat capacity, nor the amount of heat required to maintain the heated wash-off liquor and beads at the final temperature.

As Table 3 shows, in the case of the reduction clearing process, although no heat would be consumed during the cold water rinse stage, a large amount of energy would nevertheless be consumed in the other three stages of the process in heating the water that would be used in both 40 °C rinse stages and the NaOH/$Na_2S_2O_4$

Table 3
Amount of heat energy required.

Reduction clear				Bead wash-off			
Stage	Temp./°C	Liquor ratio[a]	Q/kJ	Stage	Temp./°C	Liquor/bead ratio[a]	Q/kJ
Rinse	40	20:1	159	Beads/ detergent	70	2:1 15:1	41 123
Na_2CO_3/ $Na_2S_2O_4$	60	20:1	327	Cold rinse	21	10:1	0
Rinse	40	20:1	159	–	–	–	–
Cold rinse	21	10:1	0	–	–	–	–
Total			645				144

[a] The calculation assumes a 100 g fibre mass resulting in 2 kg of water in the case of a 20:1 L:R and 200 g water in the case of a 2:1 L:R as well as 1.5 kg beads in the case of a 15:1 bead:fibre ratio.

stage, since each stage involved the use of a 20:1 liquor ratio. Table 3 shows that a total of 645 kJ of heat energy would be consumed during the reduction clearing process. In the case of the two bead wash-off processes, Table 3 reveals that again, whilst no heat energy would be used in the cold rinse stage of the bead wash-off, considerably less heat energy would be used in the 70 °C bead wash-off stage as this employed only a 2:1 water:fibre ratio rather than the 20:1 liquor ratio that was used in reduction clearing and, therefore, there was a smaller mass of water that required heating. Nevertheless, although less water was used in the bead stage, the beads themselves required heating. A 15:1 bead:fibre ratio was employed in the bead stage of the process, this being only just smaller than the 20:1 water:fibre ratio used in the $NaOH/Na_2S_2O_4$ stage of the reduction clear process; indeed, according to the assumptions upon which the calculations were made (i.e. a 100 g fibre sample), then the respective masses of water and beads which require heating are 2 kg of water, in the case of a 20:1 water:fibre ratio and 1.5 kg beads in the case of a 15:1 bead:fibre ratio. As nylon has a much lower specific heat capacity than water ($1.67\ kJ\ kg^{-1}\ K^{-1}$ compared to $4.18\ kJ\ kg^{-1}\ K^{-1}$), considerably less energy is needed to heat the 1.5 kg of nylon beads to 70 °C than is needed to heat the greater mass (2 kg) of water to 60 °C, which explains why, for the bead stage of wash-off, heating 1.5 kg of beads from 21 to 70 °C requires some 123 kJ whereas to raise 2.0 kg of water to 60 °C requires 327 kJ (Table 3). The total amount of heat energy consumed in the bead wash-off process would be 144 kJ (Table 3), this being a just over 20% of that used in the reduction clearing process.

4. Conclusions

Comparison of the colorimetric data obtained for dyeings which had been reduction cleared with that secured for dyeings which had been washed-off using nylon beads at 70 °C in the presence of both *Sandozin NIN* and *ECE detergent* shows that while the colour strength of the washed-off samples was slightly lower than that of the reduction cleared samples, there was no difference between the λ_{max} of the washed-off and reduction cleared dyeings. The change in shade and staining results obtained for dyeings which had been reduction cleared with those secured for dyeings which had been washed-off using nylon beads at 70 °C in the presence of both *Sandozin NIN* and *ECE detergent* shows that the washed-off dyeings displayed similar levels of fastness to repeated washing at 60 °C to that of their reduction cleared counterparts.

Thus, in terms of fastness and colorimetric characteristics, the results obtained suggest that the traditional, four-stage reduction clearing treatment using aq alkaline $Na_2S_2O_4$ can be replaced by a two-stage, bead wash-off with detergent at 70 °C. From a practical perspective, the use of the detergent-based, bead wash-off process would not only negate the requirement for three changes in pH [acidic dyebath (~pH 5) to alkaline reduction clear (~pH 12) to neutralisation with aq. CH_3COOH] and also result in the consumption of lower amounts of water and chemicals; the absence of dithionite would avoid the environmentally unacceptable generation of aromatic amines in the case of the reduction clearing of azo dyes. Adsorption of vagrant dye by the beads might also potentially enable a major reduction to be achieved in terms of the BOD, COD, TOC and suspended solids which can be generated during a typical traditional reduction clearing treatment for disperse dyes on polyester. Calculations indicate that considerably less heat energy would be consumed in washing-off dyeings using the bead processes than reduction clearing not only because two, rather than four stages were involved but, more importantly, because the bead stage uses only a 2:1 water:fibre ratio rather than the 20:1 liquor ratio employed in the reduction clear process and the much lower specific heat capacity of nylon than water means that much less heat is required to heat the nylon beads.

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